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INTRAMOLECULAR CONVERSION OF A FIVE-MEMBERED IRIDACYCLE  
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OF CHEMISTRY AND BIOCHEMISTR P A CHETCUTI ET AL

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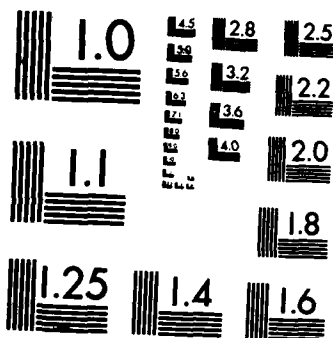
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Thermolysis of the metallacycles <u>1a</u> and <u>1b</u> in refluxing toluene for 24 hours results in loss of CO <sub>2</sub> and the formation of a product characterized by the formal oxidative addition of the 16-electron Ir(I) metal fragment (CpIrPPh <sub>3</sub> ) into the nitrile triple bond, generating the kinetically very stable side-bonded nitrile complexes <u>2a</u> and <u>2b</u> , in high yield. An X-ray diffraction study <u>was undertaken</u> of <u>2a</u> confirming its structure as that containing a Ir(III)-C≡N metallacycle.		

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**TECHNICAL REPORT NO. 125**

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Three-Membered Counterpart by CO<sub>2</sub> Extrusion**

**by**

**Peter A. Chetcuti, Carolyn B. Knobler and M. Frederick Hawthorne\***

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Intramolecular Conversion of a 5-Membered Iridacycle  
to a 3-Membered Counterpart by CO<sub>2</sub> Extrusion

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Abstract

Thermolysis of the metallacycles 1a and 1b in refluxing toluene for 24 hours results in loss of CO<sub>2</sub> and the formation of a product characterized by the formal oxidative addition of the 16-electron Ir(I) metal fragment "CpIrPPH<sub>3</sub>" into the nitrile triple bond, generating the kinetically very stable side-bonded nitrile complexes 2a and 2b, in high yield. An X-ray diffraction study was undertaken of 2a confirming its structure as that containing a Ir(III)-C≡N metallacycle.

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We have been investigating the reactivity of metallacycles generated by the cycloaddition of aryl nitrile oxides to low valent metal carbonyl complexes.<sup>1</sup> We wish to report the formation of side-bonded nitrile complexes whose chemical characteristics appear to be more readily attributed to the result of oxidative addition across the nitrile triple bond by a metal fragment than by  $\pi$ -complexation of a nitrile to a low valent metal.

Thermolysis of 1a and 1b<sup>2</sup> in boiling toluene for 24 hours leads to the formation of the remarkably stable 2a and 2b, respectively, with extrusion of CO<sub>2</sub>. All <sup>1</sup>H, <sup>19</sup>F and <sup>31</sup>P NMR data, as well as elemental analyses, are consistent with the structures shown for 2a and 2b.<sup>3</sup> The structure of 2a was also confirmed by an X-ray diffraction study described below. The IR spectra of 2a and 2b exhibit

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Scheme  
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a CN stretching frequency at 1758 cm<sup>-1</sup> and 1756 cm<sup>-1</sup>, respectively, a decrease of 472 cm<sup>-1</sup> and 468 cm<sup>-1</sup> from the corresponding free nitriles. Similar large decreases in the CN stretching frequencies have been observed in other complexes which are believed to contain side-bonded nitriles,<sup>4-8</sup> as opposed to the more common mode of nitrile coordination which occurs by  $\sigma$ -bonding through the nitrile nitrogen lone electron pair.<sup>9</sup> In order to establish whether the formation of free nitrile occurred by decomposition of 1, to generate the 16-electron metal fragment "CpIrPPh<sub>3</sub>" which then coordinates free nitrile, or if an intramolecular mechanism was involved, 1b was decomposed in the presence of a 20-fold excess of p-ClC<sub>6</sub>H<sub>4</sub>CN. If nitrile formation occurred by the former mechanism, 2a would be the predominant product, whereas if an intramolecular process was involved, then compound 2b should be obtained. Both <sup>31</sup>P and <sup>19</sup>F NMR identified 2b as the predominant product (80% yield by NMR); no resonance in the <sup>31</sup>P NMR was observed for 2a. This result indicated that no nitrile exchange had occurred and that the formation of 2 involved an intramolecular process. The <sup>19</sup>F NMR of the products of decomposition of 1b gave two resonances, one of which corresponded to 2b and the other to free p-FC<sub>6</sub>H<sub>4</sub>CN. The yield of p-FC<sub>6</sub>H<sub>4</sub>CN was 9% by NMR in the absence of p-ClC<sub>6</sub>H<sub>4</sub>CN and 20% in the presence of p-ClC<sub>6</sub>H<sub>4</sub>CN; the <sup>31</sup>P NMR contained a minor resonance at 17.09 ppm together with the major resonance due to 1b in both cases. The <sup>1</sup>H NMR spectrum of the reaction products gave no evidence of hydrides which could be formed as

a result of C-H oxidative addition of the solvent or intramolecular hydride abstraction. The nature of the minor product resulting from loss of  $p\text{-FC}_6\text{H}_4\text{CN}$  from **1b** and having a  $^{31}\text{P}$  NMR resonance at 17.09 ppm was not determined.

The stability of **2a** and **2b** and their mode of formation strongly support a product which would result from formal oxidative addition of an Ir(I) 16-electron fragment to the CN triple bond thereby generating an Ir(III)  $\text{Ir}-\text{C}\equiv\text{N}$  metallacycle, rather than simple  $\pi$ -complexation of a nitrile to a metal center. The nitrile ligands of **2a** and **2b** are not easily displaced. In contrast, the nitrile ligand of the side-bonded nitrile complex  $(\text{PPh}_3)_2\text{Pt}(\pi\text{-CF}_3\text{CN})$ ,<sup>8</sup> is readily displaced by CO and diphenylacetylene at room temperature. The only side-bonded nitrile complexes comparable to **2a** and **2b** are molybdenocene nitrile complexes<sup>4</sup> for which no crystallographic study is available to confirm their structure.

An X-ray diffraction study was undertaken of compound **2a**,<sup>10</sup> which established the nitrile ligand to be side-bonded to the Ir (Figure 1). The Ir-C(6) bond length is 2.11(2) Å, which is the expected length for an Ir(III)-C bond;<sup>11,12</sup> the Ir-N bond distance is 2.17(2) Å which represents a long Ir-N single bond.<sup>13,14</sup> The C(6)-N bond distance is 1.23(3) Å, which represents a lengthening of 0.08 Å to that of the free nitrile. No structural information is available to compare this C-N bond distance with other side-bonded nitrile complexes; a number of acetylene  $\eta^2$  complexes have been structurally characterized and are observed to undergo large reductions in the C-C stretching frequencies and accompanying lengthening of the C-C bond.<sup>14,15</sup> The average increase in the C-C bond length on coordination is 0.08 Å. The lengthening observed for the C-N distance of **2a** is of the same magnitude, suggesting a similar reduction in the bond order.

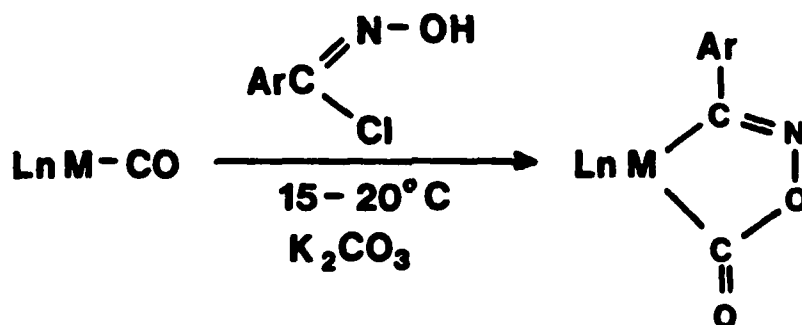
From the intramolecular mode of formation of the nitrile complexes **2a** and **2b**, and their great chemical stability when compared to other side-bonded nitrile complexes, it appears that **2a** and **2b** are best described as formal Ir(III) metallacycles.

**Acknowledgements:** We are grateful to the Office of Naval Research for the support research (Contract No. N00014-76-C-0390). We also thank Johnson-Matthey Corporation for a generous gift of iridium chloride.

**Supplementary Material Available:** Tables of positional and thermal parameters, interatomic distances and angles, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

## References

1. We have synthesized a number of metallacycles by cycloaddition of aryl nitrile oxides with low valent metal carbonyl complexes. A preliminary communication has been published (Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. J. Am. Chem. Soc. 1983 105, 3370.) and a complete report of this synthetic route to these metallacycles and their reactivity will be submitted shortly; the general reaction is outlined below.



Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>-; 2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>-; *p*-FC<sub>6</sub>H<sub>4</sub>-  
 Metallacycle yields vary between 60 and 80%.

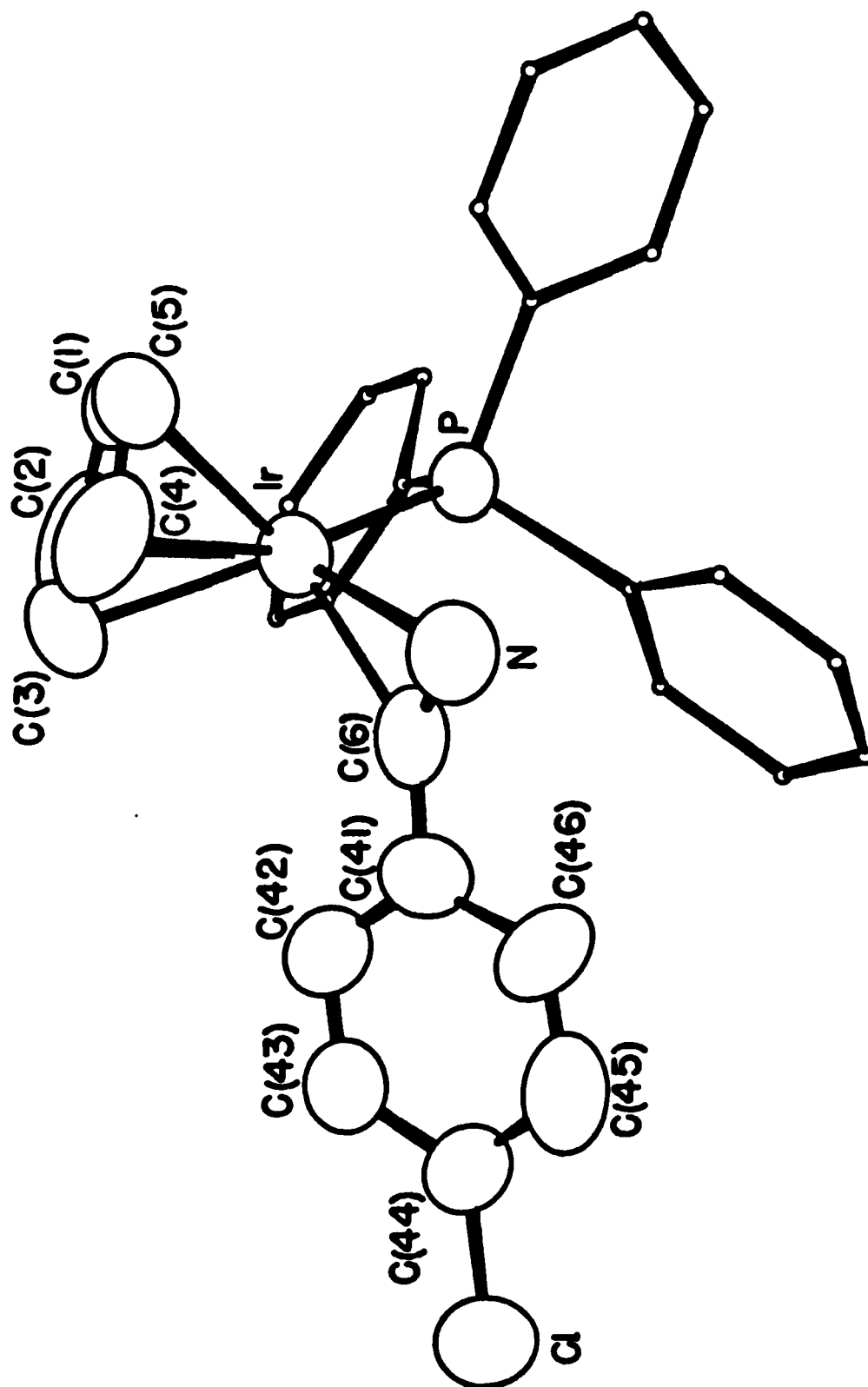
2. Selected data for 1a and 1b (full details will be reported elsewhere<sup>1</sup>).  
 1a: Anal. Calc. for C<sub>31</sub>H<sub>24</sub>ClIrNO<sub>2</sub>P: C, 53.17; H, 3.46; Ir, 27.45; N, 2.00; P, 4.42. Found: C, 52.92; H, 3.57; Ir, 27.12; N, 1.91; P, 4.33.  
<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.37-7.15 (complex multiplets, 19 H), 5.39 (d, 5 H, J = 1.0 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ -2.22.  
 1b: Anal. Calc. for C<sub>31</sub>H<sub>24</sub>FNO<sub>2</sub>PIr: C, 54.37; H, 3.54; Ir, 28.07; N, 2.05; P, 4.52. Found: C, 54.12; H, 3.66; Ir, 27.92; N, 2.01; P, 4.44.  
<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.46-6.74 (complex multiplets, 19 H), 5.393 (d, 5 H, J = 0.88 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>): δ -2.09.
3. Selected data for 2a and 2b (full details will be reported elsewhere<sup>1</sup>).  
 2a: Anal. Calc. for C<sub>30</sub>H<sub>24</sub>ClIrNP: C, 54.83; H, 3.69; N, 2.13; P, 4.71. Found: C, 54.66; H, 3.60; N, 1.97; P, 4.08. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.15-8.24 (complex multiplets, 19 H), 5.90 (d, 5 H, J = 1.46 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 16.56.  
 2b: Anal. Calc. for C<sub>30</sub>H<sub>24</sub>FIrNP: C, 56.23; H, 3.78; Ir, 29.99; N, 2.19; P, 4.83. Found: C, 55.70; H, 3.94; Ir, 29.42; N, 2.15; P, 4.71. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 4.67-6.82 (complex multiplets, 19 H), 5.267 (d, 5 H, J = 1.2 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>): δ 16.29.

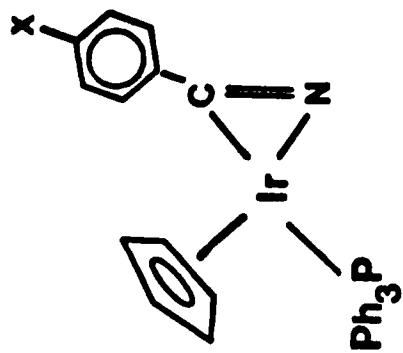
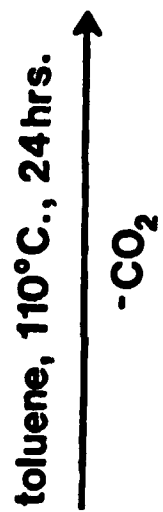
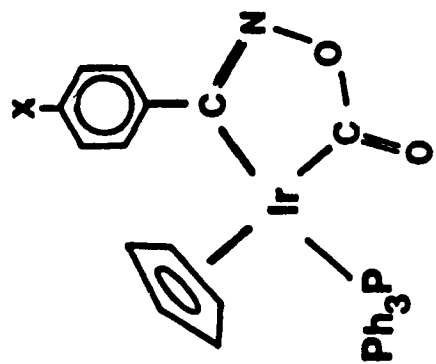


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10. Crystal data for 2a:  $C_{30}H_{24}ClIrNP$ : Mr = 657.1; yellow-brown parallel-piped; orthorhombic; space group Pcan (standard setting, Pbcn); a = 10.638(2) Å, b = 14.298(3) Å, c = 33.310(5) Å; V = 5066 Å<sup>3</sup>; Z = 8; D(calc.) = 1.72 g cm<sup>-3</sup>. A total of 4254 unique reflections were collected of which 2495 were considered observed ( $I > 3\sigma(I)$ ) and were used in subsequent calculations (Hübler diffractometer built by Professor C. E. Strouse of this department; MoK<sub>α</sub> radiation; graphite monochromator;  $\lambda$  = 0.7107 Å;  $\theta$ -2 $\theta$  scan;  $0 < 2\theta < 54^\circ$ ;  $\mu$  = 5.733 cm<sup>-1</sup>). The structure was solved by the heavy atom method using SHELX 76. In the final least-squares cycle, based on F, 307 parameters were refined including positional and anisotropic thermal parameters for one Ir, thirty C, one Cl, one N and one P. Refinement is currently at R = 0.077 and R<sub>w</sub> = 0.086. The goodness of fit is 2.26
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Figure Caption

Figure 1: ORTEP drawing of  $[(C_5H_5)(PPh_3)Ir(\eta^2-NCC_6H_4Cl)]$  (2a).  
Hydrogen atoms have been omitted for clarity  
and phenyl groups are depicted schematically.





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